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Melamine-ZnI$_2$ as heterogeneous catalysts for efficient chemical fixation of carbon dioxide to cyclic carbonates

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Abstract: In this contribution, the combination of melamine with Lewis acid ZnI$_2$ was developed as heterogeneous dual catalysts for the cycloaddition of carbon dioxide with epoxides yielding the corresponding cyclic carbonates. With molar ratio of 1:3.3 of ZnI$_2$ to melamine, high yield (96%) and selectivity (99%) of propylene carbonate was obtained at 150 °C and 3.0 MPa for 4.0 h. The binary catalysts were also effectively versatile to CO$_2$ cycloaddition to other epoxides, especially the less active epoxides such as styrene oxide and cyclohexene oxide. Additionally, the catalysts could be separated easily from the products after reaction and then reused efficiently. Furthermore, a possible synergistic catalytic mechanism was proposed, wherein, melamine played the dual roles to activate CO$_2$ and epoxide simultaneously, ZnI$_2$ activated epoxide and subsequently attacked the activated epoxide, the synergetic effects from melamine and ZnI$_2$ promoted the reaction smoothly. The binary catalysts showed the advantages of simple preparation, low cost, abundant availability and high catalytic activity for CO$_2$ chemical fixation into valuable chemicals.

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1. Introduction

Carbon dioxide has attracted great attentions as a greenhouse gas that contributes to climate change. A major source of CO_2 emission is combustion of fossil fuels such as oil and coal for the production of electricity and heat. According to information statistics, the world consumption of coal is expected to increase from now to 2030 by 49%, and accordingly, considerable attention is being focused on reducing CO_2 emission from power-plant flue-gas streams.[1] The main strategy for reduction of CO_2 emission is the carbon capture and storage (CCS) operated in fossil-fuel power stations.[2] Nonetheless, the fixation of waste CO_2 to generate valuable chemicals such as cyclic carbonates via cycloaddition of CO_2 to epoxides is an attractive alternative (Scheme 1). As the formation of cyclic carbonates is green for 100% atom efficiency, furthermore, cyclic carbonates are an important class of chemical products not only used as polar aprotic solvents, electrolytes for lithium-ion batteries, intermediates in the manufacture of fine chemicals,[3] but also used as constituents of oils and paints, and raw materials in the synthesis of polycarbonates [4] and polyurethanes.[5]
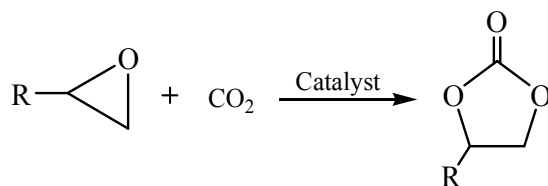
Scheme 1 Insertion of CO_2 into the epoxides for the synthesis of cyclic carbonates.

Currently, a wide range of homogeneous catalysts have been developed for the insertion of carbon dioxide into epoxides.[6] North and co-workers developed an exceptionally active bimetallic aluminium (salen) compound, which coupled with *n*-Bu$_4$NBr co-catalyst could catalyze the insertion of CO_2 into terminal epoxides at

atmospheric pressure and room temperature.[7] Kleij's group created aluminum complex based on amino triphenolate ligand, which showed unprecedented high activity in combination with PPN-Br (PPN = bis-(triphenylphosphine)iminium) cocatalyst and the initial TOFs were up to 36000 h^{-1} at 90 °C and 1.0 MPa.[8] A recent work reported by Cokoja et al. revealed a dual catalyst system including pentaerythritol and nucleophilic halide salts such as n-Bu$_4$NI for the cycloaddition of CO_2 with a broad range of organic epoxides, among these the propylene carbonate yield could reach 96% at 70 °C and 0.4 MPa for 16 h.[9] Although significant progress has been made, the homogeneous catalysts are undesirable in industry due to the problems such as rigorous separation and purification of the products, which may require more energy and result in the decomposition of the catalysts.[10] Thus, the development of highly efficient heterogeneous catalysts for the CO_2 cycloaddition to epoxides particularly under mild conditions is necessitated. Several types of heterogeneous catalysts, such as metal-organic frameworks,[11] functionalized polymer,[12] active species supported on natural or synthesized polymers,[13] silica,[14] SBA-15 [15] and MCM-41,[16] have been explored for the coupling reactions of epoxides with CO_2. However, these heterogeneous systems are restricted due to low activity and/or poor stability as well as the complex synthetic process for the catalysts. Hence, the exploration for heterogeneous catalysts that are simple for preparation and capable of efficiently converting CO_2 into cyclic carbonates is still highly desirable.

Melamine with Lewis basic and high nitrogen level (66% by mass)[17] was used primarily for the production of melamine resins and many industrial applications such

as for the generation of laminates, glues, adhesives, moulding compounds, coatings and flame retardants. To the best of our knowledge, there is no report on melamine as catalyst for the synthesis of cyclic carbonates. Herein, we developed a dual heterogeneous catalyst system composed of melamine and Lewis acid ZnI_2 for the CO_2 cycloaddition to several epoxides. The effects of reaction parameters such as temperature, CO_2 pressure, catalyst loading and reaction time on catalytic activity were investigated thoroughly. Moreover, the reusability of the binary Melamine-ZnI_2 catalysts was examined and the plausible reaction mechanism was proposed.

2. Results and discussion

2.1 Cocatalyst screening for the CO_2 cycloaddition to propylene oxide

The performance of melamine with various Lewis acid cocatalysts was investigated on the cycloaddition reaction of propylene oxide and CO_2, and the results are summarized in Table 1. Almost no product was detected when melamine or ZnI_2 was used alone (entries 1 and 2). Nevertheless, the catalytic behaviors of melamine combined with different Lewis acid cocatalyst varied considerably. The reaction almost did not take place or very little conversions were obtained over melamine with Cu^{2+}, Mg^{2+}, Cd^{2+} or Fe^{3+} (entries 8-11). It has been recognized profoundly that zinc halide played essential role for the coupling reaction.[18] Similarly, melamine combined with zinc halide showed significant activity than other metallic halides in accordance with the stronger Lewis acidity of Zn^{2+} (entries 3-5). When ZnO or $Zn(NO_3)_2$ substituted for zinc halide, the corresponding catalyst system showed very poor

activities (entries 6 and 7) exhibiting the significant influence of anion. It was

revealed that the catalytic activity improved with the increase of halide anion leaving

ability at the order of $I^- > Br^- > Cl^-$. With prolonging the reaction time to 6 h, the

yield of propylene carbonate could reach 98% with high selectivity over

Melamine-ZnI_2 catalysts (entry 12). Thus, ZnI_2 was selected with melamine for

further investigation under solvent-free conditions.

Table 1 Screening of Lewis acid in combination with melamine for the cycloaddition reaction[a]


| | | PO | | | PC |

Entry	Catalytic system	Reaction results[b]	
		Y_{PC} (%)	S_{PC} (%)
1	Melamine	trace	—
2	ZnI_2	trace	—
3	Melamine -$ZnCl_2$	37	≥ 98
4	Melamine -$ZnBr_2$	46	≥ 98
5	Melamine -ZnI_2	69	≥ 98
6	Melamine -ZnO	trace	—
7	Melamine -$Zn(NO_3)_2$	trace	—
8	Melamine -$CuCl_2$	5	≥ 97
9	Melamine -$MgCl_2$	trace	—
10	Melamine -$CdCl_2$	trace	—
11	Melamine -$FeCl_3$	12	≥ 97
12[c]	Melamine -ZnI_2	98	≥ 98

[a] Reaction conditions: PO 34.5 mmol, Melamine 0.24 mmol, Lewis acid 0.08 mmol, T = 140 °C, P (CO_2) = 3.0 MPa, t = 3.0 h. [b] Y_{PC}: PC yield; S_{PC}: PC selectivity; all based on GC analysis. [c] t = 6.0 h.

2.2 Effect of reaction temperature on Melamine-ZnI$_2$ catalytic performance

Subsequently, the effects of some parameters on the catalytic activity of Melamine-ZnI$_2$ were investigated. The dependence of PC yield and selectivity on reaction temperature is shown in Fig. 1. The temperature had a pronounced positive effect on the coupling reaction from 110 to 150 °C, correspondingly, the PC yield was enhanced from 35% to 87% and PC selectivity all kept above 98%. When the reaction temperature was further increased higher than 150 °C, the PC yield improved slightly. To our delight, the temperature did not affect the PC selectivity. Hence, the optimal temperature for the reaction of PC synthesis was 150 °C.
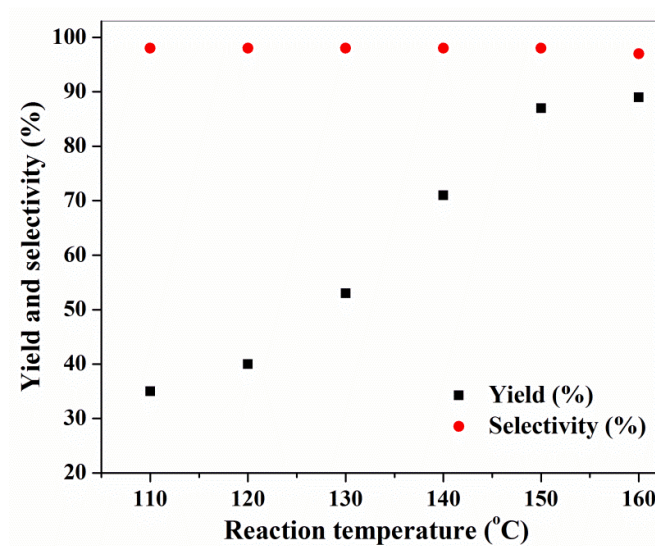

Fig. 1 Effect of the reaction temperature on the yield and selectivity of PC. Conditions: PO 34.5 mmol, Melamine 0.24 mmol, Lewis acid 0.08 mmol, P (CO$_2$) = 3.0 MPa, t = 3.0 h.

2.3 Effect of CO$_2$ pressure on Melamine-ZnI$_2$ catalytic performance

Generally, a significant drawback associated with CO$_2$ as reagent or reaction medium in organic synthesis is the potential dangers operated at high pressures.[19] The effect of CO$_2$ pressure on the cycloaddition to PO in the presence of Melamine-ZnI$_2$ catalysts

was also investigated. As depicted in Fig. 2, the PC yield increased dramatically in the low-pressure range of 1.0-3.0 MPa, whereas, the increased CO_2 pressure from 3.0 MPa to 4.0 MPa resulted in slight changes in PC yield. According to the previous literatures,[18c,20] the possible reason could be ascribed to the phase behavior of CO_2-PO system which led to the effect of pressure on the concentrations of CO_2 and epoxide. There were three phases in the reaction system including the bottom PO-rich liquid phase, catalyst-rich solid phase and the top CO_2-rich gas phase, and the reaction mainly took place in the PO-catalyst interface.[19,21] The initial increase of CO_2 pressure resulted in the enhanced concentration of CO_2 in the liquid phase, thus improving PC yield remarkably. However, the yield no longer increased with the pressure beyond 3.0 MPa up to 4.0 MPa, which was possibly explained that the higher pressure extracted a certain amount of PO into the gas phase, and caused the reduction of PO concentration in the vicinity of the catalyst in the liquid phase.[22] Conclusively, 3.0 MPa was the optimal CO_2 pressure for PC synthesis.
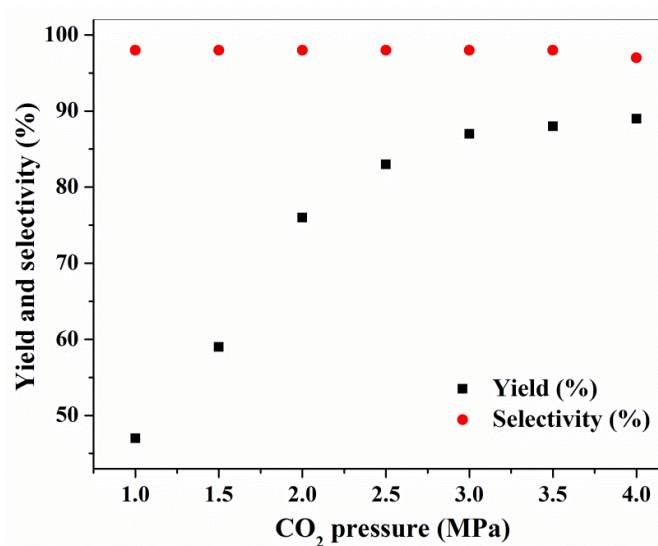
**Fig. 2** Effect of the reaction pressure on the cycloaddition reaction of PO. Reaction conditions: PO

34.5 mmol, Melamine 0.24 mmol, Lewis acid 0.08 mmol, T = 150 °C, t = 3.0 h.

2.4 Effect of catalyst loadings on Melamine-ZnI$_2$ catalytic performance

The influence of the catalyst loadings on the CO_2 cycloaddition to PO was also investigated in Table 2. The results showed that the catalytic activity of the binary system strongly depended on the ratios of the catalysts. First, we fixed the molar amount of ZnI$_2$ at 0.08 mmol and varied the amount of melamine from 0.08 to 0.40 mmol, the yield of PC increased from 58% to 81% (entries 1-3), whereas further improved melamine amount to 0.48 mmol, the PC yield increased slightly (entry 4). At 0.40 mmol melamine (1.15 mol% of PO), the amounts of ZnI$_2$ were varied from 0.04 to 0.16 mmol (entries 3, 5-8). PC yield could reach optimal 93% at 0.12 mmol ZnI$_2$ (0.35 mol% of PO) (entry 7). Thus, the optimum ZnI$_2$-Melamine molar ratio was 1:3.3 at the optimal catalyst loading of 1.5 mol% PO. Moreover, the reaction even proceeded smoothly under lower reaction temperature of 110 °C, and ≥94% PC yield could be obtained or even with lower catalyst amount but at the expense of longer reaction time (entries 9 and 10).

Table 2 Influence of catalyst loadings on the formation of PC from PO and CO_2[a]

Entry	Catalytic system		Reaction results[b]	
	Melamine (mmol)	ZnI$_2$ (mmol)	Y$_{PC}$ (%)	S$_{PC}$ (%)
1	0.08	0.08	58	99
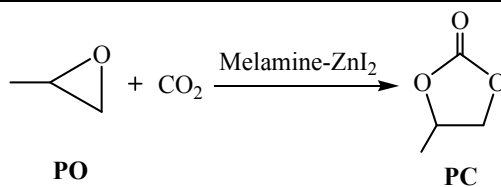
2	0.24	0.08	73	99
3	0.40	0.08	81	99
4	0.48	0.08	83	98
5	0.40	0.04	64	99
6	0.40	0.06	75	99
7	0.40	0.12	93	99
8	0.40	0.16	94	98
9[c]	0.40	0.12	95	98
10[d]	0.24	0.06	94	97

[a] Reaction conditions: PO 34.5 mmol, T = 150 °C, P (CO_2) = 3.0 MPa, t = 3.0 h. [b] Y_{PC}: PC yield; S_{PC}: PC selectivity; all based on GC analysis. [c] 110 °C, 12 h. [d] 110 °C, 16 h.

### 2.5 Effect of reaction time on Melamine-ZnI$_2$ catalytic performance

Additionally, the dependence of PC yield and selectivity on the reaction time was also evaluated. As shown in Fig. 3, PC yield enhanced from 42 to 98% when the reaction duration was extended from 1 h to 6 h. The cycloaddition reaction proceeded rapidly within the first 4 h and reached 96% PC yield. Further prolonging the reaction time resulted in only a slight rise in PC yield. Again, the selectivity of PC stayed above 99 % throughout. Hence, 4 h was chosen as the optimum reaction time.
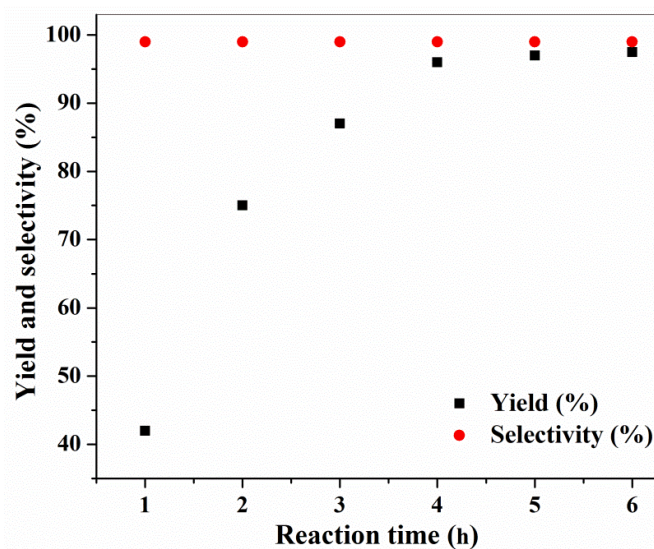
Fig. 3 Dependence of PC yield and selectivity on reaction time. Conditions: PO 34.5 mmol, Melamine 0.40 mmol, ZnI_2 0.12 mmol, $T = 150$ °C, $P (CO_2) = 3.0$ MPa.

2.6 Reusability of Melamine-ZnI_2 catalysts

To the best of our knowledge, the recyclability of a catalyst plays an important role in practical application.[9] In order to examine the reusability of the binary Melamine -ZnI_2 catalytic system, the coupling reaction of CO_2 with PO was repeated under the optimum reaction conditions (150 °C, 3.0 MPa, 4.0 h). As shown in Fig. 4, no obvious decrease of PC yield was observed after four recycles and the selectivity to PC stayed above 99%, indicating that Melamine-ZnI_2 catalysts exhibit good stability for CO_2 cycloaddition reaction to PO. Whereas, it was worth noting that in the third recycle, additional 1 wt% ZnI_2 was added because a small amount of ZnI_2 was dissolved in the PC product, resulting in the slight loss of ZnI_2.
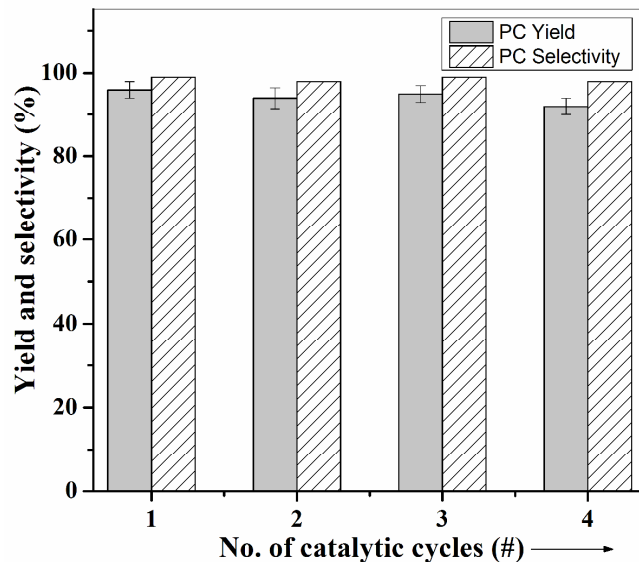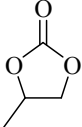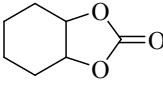
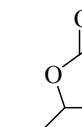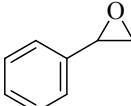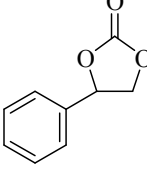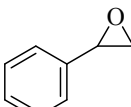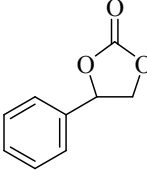**Fig. 4** Recyclability of the catalysts. Conditions: PO 34.5 mmol, Melamine 0.40 mmol, ZnI$_2$ 0.12 mmol, T = 150 °C, P (CO$_2$) = 3.0 MPa, t = 4.0 h.

2.7 CO$_2$ cycloaddition to various epoxides

In order to show the potential and versatile applicability of the dual catalysts, the coupling reaction of CO$_2$ with different terminal epoxides was investigated under the optimized reaction conditions as shown in Table 3. Melamine-ZnI$_2$ catalysts were found to be efficient for the conversions of a variety of epoxides to the corresponding cyclic carbonates with high yield and selectivity ($\geq$ 97%) (entries 1-6). Among the epoxides surveyed, PO was the most reactive (entry 1), with the increase of the steric hindrance from side 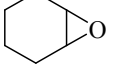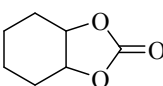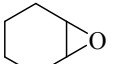chain substituent of substrate, the catalytic activity was impeded. Nonetheless, it was worth mentioning that the corresponding carbonates from styrene oxide and cyclohexene oxide were obtained in excellent yields after longer reaction time (entries 4 and 6), although styrene oxide and cyclohexene oxide were known to be notoriously difficult to undergo CO$_2$ cycloaddition due to the higher hindrance originated from the two rings. Thus the extension to various epoxides reflected the

outstanding universality of the binary catalysts.

Table 3 Coupling reaction of CO_2 with various epoxides catalyzed by Melamine -ZnI_2[a]

Entry	Epoxide	Product	Time (h)	Reaction results[b]	
				Y_{PC} (%)	S_{PC} (%)
1			4	96	99
2			4	92	99
3			6	88	98
4			8	93	97
5			6	81	99
6			10	90	98

[a] Reaction conditions: epoxide 34.5 mmol, Melamine 0.40 mmol, ZnI_2 0.12 mmol, $T = 150$ °C, P (CO_2) = 3.0 MPa. [b] Y_{PC}: PC yield; S_{PC}: PC selectivity; all based on GC analysis.

2.8 Proposed reaction mechanism

Previous reports on cyclic carbonate synthesis from CO_2 and epoxides suggested the dual requirements of Lewis acid and Lewis base sites for the activation of epoxide and CO_2, respectively.[18a] Moreover, it was well recognized that epoxides could be activated by zinc halides to form the zinc-epoxide adduct [23] and CO_2 could be

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activated by amine.[24] In order to gain a deeper insight into the reaction mechanism over Melamine-ZnI$_2$ catalysts, FT-IR spectra were employed to verify the CO_2 activation by melamine.[25] As shown in Fig. 5, there appeared a new band centered at 1791.4 cm^{-1}, which correspond to the new asymmetric C=O vibration of carbamate salt (Scheme 2), implying the activation of CO_2 by melamine (MA) consistent with the previous report.[26] The dual Melamine-ZnI$_2$ catalysts showed the synergetic effects on the enhanced activity for the chemical fixation of CO_2 to epoxide, shown in Scheme 3. Firstly, melamine played the role of Lewis base to activate CO_2 forming a zwitterionic adduct as well as –NH$_2$ groups in MA coordinated with the oxygen of epoxide through hydrogen bonds. Moreover, ZnI$_2$ also attacked the oxygen of epoxide to form the zinc-epoxide adduct,[21a] resulting in the both activations to epoxide molecule. And secondly, alkaline N atom in MA and the I$^-$ anion as Lewis bases nucleophilicly attacked on the less sterically hindered β-carbon atom of epoxide, followed by the ring-opening of PO and led to the formation of the intermediate 1. Subsequently, the MA simultaneously coordinated with CO_2, affording a carbamate salt 2 (Scheme 2) as the activated species of CO_2.[27] Thereafter, the intermediate 1 made nucleophilic attack on the carbamate salt 2 to produce the new alkyl carbonate compound 3, simultaneously leaving one melamine. Finally, by the subsequent intramolecular ring-closure, the cyclic carbonate could be formed and the catalysts were regenerated. The synergetic catalysis roles played by melamine and ZnI$_2$ made the reaction proceed effectively.
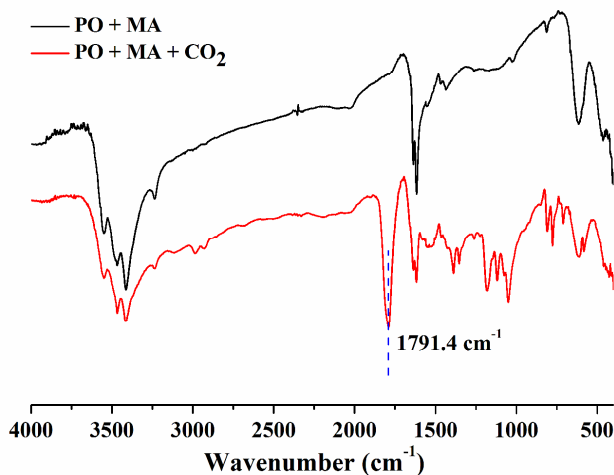
Fig. 5 FT-IR spectra of CO_2 activated by melamine. Conditions: epoxide 34.5 mmol, Melamine 0.40 mmol, P (CO_2) = 3.0 MPa, T = 140 °C, t = 30 min.
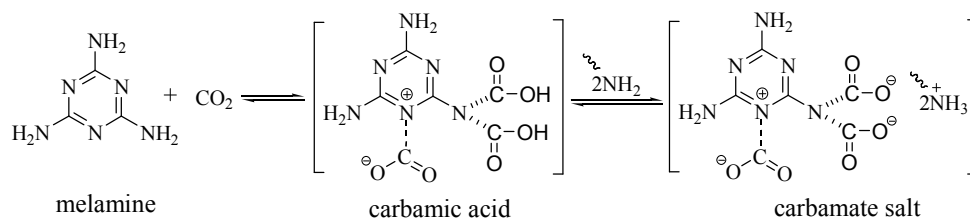
Scheme 2 Structure and formation of carbamate salt 2.
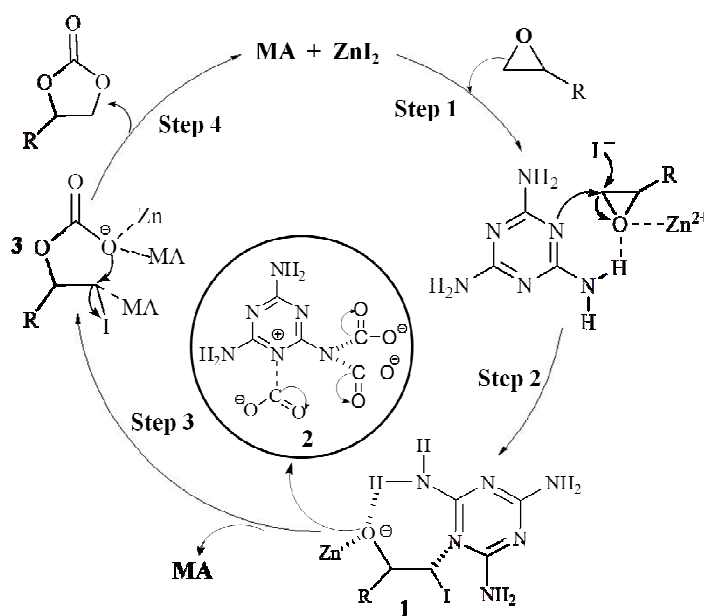
Scheme 3 Proposed mechanism for MA-ZnI_2 catalyzed cycloaddition reaction of CO_2 and epoxide.

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MA represented Melamine.

3. Experimental

3.1. Materials and instruments

The reagents and chemicals (analytic grade unless otherwise stated) were purchased from Sinopharm Chemical Reagent Co. Ltd.. Carbon dioxide with 99.99% purity was purchased from Harbin Qinghua Industrial gases Co. Ltd.. Propylene oxide (99%), 1,2-butylene oxide, styrene oxide, cyclohexene oxide were purchased from Beijing InnoChem Science & Technology Co., Ltd.. Melamine (98%), ZnI_2 ($\geq$98%) were purchased from Adamas Reagent Co., Ltd..

FT-IR spectra were measured on a PerkinElmer Spectrum 100 FT-IR Spectrometer. GC analyses were performed on Agilent GC-7890A equipped with capillary column (Agilent 19091J-413).

3.2. Typical procedure for the CO_2 cycloaddition reaction to propylene oxide

The cycloaddition reaction of propylene oxide (PO) and CO_2 was conducted in 50 mL high pressure stainless-steel autoclave that equipped with a magnetic stirring bar. In a typical run, the reactor was charged with a certain amount of Melamine-ZnI_2 catalysts and PO (34.5 mmol) successively, then the reactor was heated using an oil bath. At fixed reaction temperature, CO_2 was introduced into the reactor to a certain pressure, then the autoclave was heated at that temperature for a designated period of time. After the reaction was completed, the reactor was cooled to 0 °C in ice-water bath, and the remaining CO_2 was released. The catalysts were separated from the system by

centrifugalization, then washed with ethyl acetate (3×5 mL), dried under vacuum and reused for another run. The products were analyzed on GC with a flame ionization detector.

4. Conclusions

In summary, the novel binary Melamine-ZnI_2 catalysts were developed and exhibited highly catalytic activity toward the CO_2 cycloaddition to various epoxides without using additional solvents. Melamine played the dual roles to activate CO_2 and PO, and ZnI_2 activated the epoxide and subsequently attacked the activated epoxide. The synergetic effects from melamine and ZnI_2 promoted the reaction effectively. Compared with the previous heterogeneous catalysts, the catalysts used in this study were simple, low-cost, innocuous to prepare. Moreover, the catalysts showed good recyclability and after four runs there was almost no loss of catalytic activity.

Acknowledgements

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Graphic Abstract

Melamine-ZnI$_2$ as heterogeneous catalysts showed high activity and versatility for cycloaddition of CO_2 to epoxides due to the synergistic effects.